

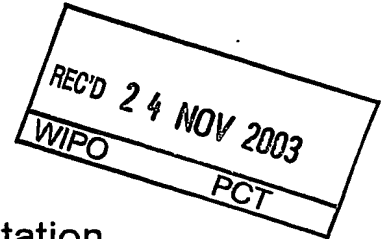
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**Patentanmeldung Nr. Patent application No. Demande de brevet n°**

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Polymers Australia PTY Limited  
32 Business Park Drive  
Notting Hill, VIC 3168  
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Process for the preparation of polyolefin nanocomposites

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**Process for the preparation of polyolefin nanocomposites**

The present invention relates to a novel process for the preparation of a polyolefin nanocomposite which comprises melt mixing a mixture of a polyolefin, a filler and a non-ionic surfactant. A further embodiment of the present invention is the use of a non-ionic surfactant to intercalate and exfoliate a filler and disperse the filler in a polyolefin matrix to form a nanocomposite. A further embodiment of the present invention is a nanocomposite comprising a) a polyolefin which is susceptible to oxidative, thermal or light-induced degradation, b) a filler, c) a non-ionic surfactant, and d) an additive selected from the group consisting of phenolic antioxidants, light-stabilizers, processing stabilizers, solvents, pigments, dyes, plasticizers, compatibilizers, toughening agents, thixotropic agents, levelling assistants and metal passivators or mixtures thereof.

There is a substantial recent literature on organic-inorganic nanocomposites based on clays or layered silicates such as montmorillonite and synthetic polymers. Polyolefin nanocomposites have been prepared from organic modified clays. The clays used are generally modified with long chain alkyl or dialkyl ammonium ions or amines or in a few cases other onium ions, like for example phosphonium. The ammonium ion/amine additives are usually incorporated into the clay structure by a separate solution intercalation step.

These conventional organic modified clays have a number of disadvantages when used for the preparation of polyolefin nanocomposites. Ammonium salts are thermally unstable at temperatures used in polyolefin processing or may be otherwise reactive under processing conditions. The clays cannot be directly dispersed into commercial polyolefins to form stable nanocomposites. Although, there are a few reports that such organic modified clays may be directly dispersed into polyolefins to form nanocomposites by intensive mixing. However, the exfoliated structures formed in this way are generally thought not to be stable and may re-aggregate during subsequent melt processing operations like for example injection moulding.

Polyolefin nanocomposite formation by melt processing has thus required use of an additional additive, most often a polypropylene-graft-maleic anhydride, which in working examples is present as major component of the final product.

A. Okada et al., *Macromolecules* 1997, 30, 6333 – 6338 or U.S. 5,973,053 disclose that a polypropylene nanocomposite is obtained when a clay, premodified with octadecylammonium salts, is compounded with polypropylene in the presence of polyolefin oligomers containing polar functionality, for example polypropylene-graft-maleic anhydride.

U.S. 5,939,184 discloses the formation of polypropylene nanocomposites based on alkyl ammonium modified clays and a polar graft polyolefin or an olefin copolymer which is typically used in excess of the amount of clay.

WO-A-99/07790 discloses a nanocomposite material on the basis of a clay having a layered structure and a cation exchange capacity of from 30 to 250 milliequivalents per 100 gram, a polymeric matrix and a block copolymer or a graft copolymer, which block copolymer or graft copolymer comprises one or more first structural units (A), which are compatible with the clay, and one or more second structural units (B), which are compatible with the polymeric matrix. Specific examples of such block copolymers are block copolymers consisting of one polyethylene oxide block (PEO) and one polystyrene block (PS); one poly-4-vinylpyridine block (P4VP) and one polystyrene block (PS); one dendritic polyethylenimine block (dend-P<sub>8</sub> PEI) and one polystyrene block (PS); or a multiblock copolymer consisting of one dendritic polyethylenimine core block (dend<sub>16</sub>) functionalized with 16 octadecyl groups (block B, PE-compatible).

WO-A-00/34393 discloses a polymer-clay nanocomposite comprising (i) a melt-processible matrix polymer, (ii) a layered clay material, and (iii) a matrix polymer-compatible functionalized oligomer or polymer. A specifically disclosed example of component (iii) is for example an ammonium functionalized polycaprolactone.

WO-A-01/48080 discloses polyolefin nanocomposites based on the use of cation exchanged clay and a high molecular weight polypropylene graft maleic anhydride.

WO-A-01/85831 discloses polyolefin nanocomposites based on the use of cation exchanged clay and a polyolefin graft organic cation like for example an ammonium ion.

The use of a poly(ethylene oxide)-block-polyethylene in the preparation of a low density polyethylene nanocomposite is described by B. Liao et al. in *Polymer* 42, 10007 – 10011

(2001). These authors make no mention of the utility of the blocks in one step nanocomposite formation.

WO-A-02/00776 relates to a porous mold for use in a pressure casting process, which mold is manufactured of a polymeric material forming a matrix into which a clay and a block copolymer or a graft copolymer have been incorporated, wherein the block copolymer or graft copolymer comprises one or more first structural units (A), which are compatible with the clay, and one or more second structural units (B), which are compatible with the polymeric matrix for the manufacture of a porous filter material. A specifically disclosed example of such a block copolymer is a block copolymer consisting of one polyethylene oxide block (PEO) and one poly(methylmethacrylate) block (PMMA).

These known methods for the preparation of polyolefin nanocomposites do not in every respect satisfy the high requirements to be met, especially with regards to polyolefin mouldings which are subject to oxidative, thermal or light-induced degradation. Further properties of interest include improved heat distortion temperature, improved fire retardancy, improved gas barrier, enhanced stiffness and dimensional stability.

There is therefore still a need to find an efficient process for the preparation of polyolefin nanocomposites that does not have the disadvantages mentioned above and which allows the use of a natural filler which has not been modified before use.

The present invention therefore relates to a process for the preparation of a polyolefin nanocomposite which comprises melt mixing a mixture of a) a polyolefin, b) a filler and c) a non-ionic surfactant.

The incorporation can be carried out in any heatable container equipped with a stirrer, for example in a closed apparatus such as a kneader, mixer or stirred vessel. The incorporation is preferably carried out in an extruder or in a kneader. It is immaterial whether processing takes place in an inert atmosphere or in the presence of oxygen.

The addition of components (a), (b) and (c) can be carried out in all customary mixing machines in which the polymer is melted and mixed with the additives. Suitable machines are known to those skilled in the art. They are predominantly mixers, kneaders and extruders.

The process is preferably carried out in an extruder by introducing the additive during processing. Particularly preferred processing machines are single-screw extruders, contrarotating and corotating twin-screw extruders, planetary-gear extruders, ring extruders or cokneaders. It is also possible to use processing machines provided with at least one gas removal compartment to which a vacuum can be applied. Suitable extruders and kneaders are described, for example, in Handbuch der Kunststoffextrusion, Vol. 1, Grundlagen, Editors F. Hensen, W. Knappe, H. Potente, 1989, pp. 3-7, ISBN:3-446-14339-4; and Vol. 2 Extrusionsanlagen 1986, ISBN 3-446-14329-7. For example, the screw length is 1 - 60 screw diameters, preferably 35 - 48 screw diameters. The rotational speed of the screw is preferably 10 to 600 rotations per minute (rpm), for example 25 - 300 rpm. The maximum throughput is dependent on the screw diameter, the rotational speed and the driving force. The process of the present invention can also be carried out at a level lower than maximum throughput by varying the parameters mentioned or employing weighing machines delivering dosage amounts. If a plurality of components are added, these can be premixed or added individually.

Of interest is a process for the preparation of a polyolefin nanocomposite, wherein the filler is a natural or synthetic phyllosilicate or a mixture of such phyllosilicates like for example a layered silicate clay. Of special interest is a process for the preparation of a polyolefin nanocomposite, wherein the filler is a montmorillonite, bentonite, beidellite, mica, hectorite, saponite, nontronite, sauconite, vermiculite, ledikite, magadite, kenyaite, stevensite, volkonskoite or a mixture thereof.

Likewise of interest is a process for the preparation of a polyolefin nanocomposite, wherein the non-ionic surfactant is a block or graft copolymer containing a hydrophilic or "clayophilic" and a hydrophobic segment(s) which do not contain an onium functionality.

Preferably, a hydrophilic or "clayophilic" segment comprises multiple polar groups such as

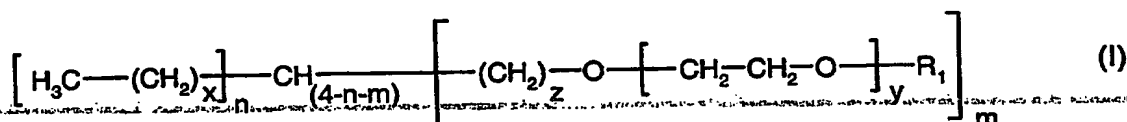
ether [-O-], amide  $\left[ -\overset{\text{O}}{\parallel}{\text{C}}-\text{N} \begin{array}{l} \diagup \\ \diagdown \end{array} \right]$ , thioamide  $\left[ -\overset{\text{S}}{\parallel}{\text{C}}-\text{N} \begin{array}{l} \diagup \\ \diagdown \end{array} \right]$ , nitrile and hydroxy in appropriate

proximity. Examples of such block grafts are poly(ethylene oxide), poly(vinyl pyrrolidone), polyacrylamide, polyacrylonitrile or poly(vinyl alcohol).

Preferably, a hydrophobic segment is "polyolefin-philic" characterized by being miscible or compatible with the polyolefin matrix phase such as a hydrocarbon segment. Alternatively, the hydrophobic segment is incompatible with the polyolefin and comprises a non-aggregating material such as a fluorocarbon, a siloxane segment or a low molecular weight methacrylate.

Of special interest is a process for the preparation of a polyolefin nanocomposite, wherein the non-ionic surfactant is a block or graft copolymer containing hydrophilic and hydrophobic segment(s) which do not contain an onium functionality, and the hydrophilic segment is a poly(ethylene oxide) block and the hydrophobic segment is a branched or unbranched polyolefin.

Likewise of special interest is a process for the preparation of a polyolefin nanocomposite, wherein the non-ionic surfactant is a sorbitan ester, a dimethylsiloxane-ethylene oxide-block copolymer, a poly(methyl methacrylate)-block-poly(oxyethylene) copolymer or a compound of the formula I



wherein

m is 1 or 2,

n is 1 or 2,

x is greater than or equal to 1,

y is greater than or equal to 1,

z is greater than or equal to 0, and

R<sub>1</sub> is hydrogen or C<sub>1</sub>-C<sub>25</sub>alkyl.

The compounds of the formula I are symmetrical or asymmetrical. This means that, if n is 2, "x" may be identical or different to the "x" in the other residue.

Alkyl having up to 25 carbon atoms is a branched or unbranched radical, for example methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl,

1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl or octadecyl.

Preferred compounds of the formula I are linear polyethylene-block-poly(ethylene oxides) of the formula I, wherein

m is 1,

n is 1,

x is 8 to 50,

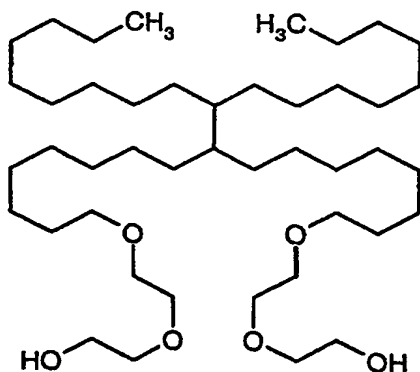
y is 1 to 32,

z is 0, and

R<sub>1</sub> is hydrogen.

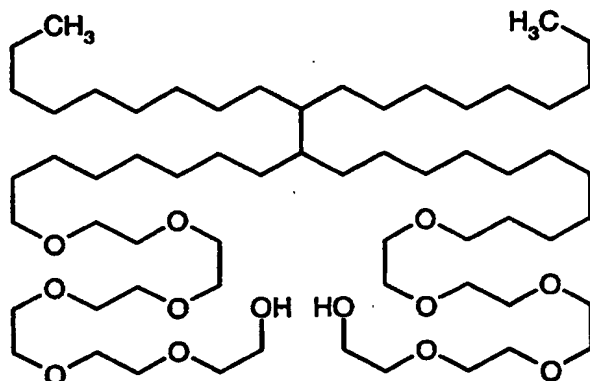
Many of these preferred linear polyethylene-block-poly(ethylene oxides) are commercially available like for example Aldrich polyethylene-block-poly(ethylene oxide) MW 1400 (average x is 50; average y is 15); Aldrich polyethylene-block-poly(ethylene oxide) MW 875 (average x is 50; average y is 4); Aldrich polyethylene-block-poly(ethylene oxide) MW 920 (average x is 32; average y is 10); Aldrich polyethylene-block-poly(ethylene oxide) MW 575 (average x is 33; average y is 2-3); Nafol 1822 + 2EO (average x is 20; average y is 2).

Especially preferred compounds of the formula I are polyethylene-block-poly(ethylene oxides) of the formula I such as for example the compounds of the formula Ia, Ib, Ic, Id or Ie which are known in the literature as DAB25, DAB50, Aduxol GA7-02, Aduxol GA8-03 and Aduxol GA10-03.

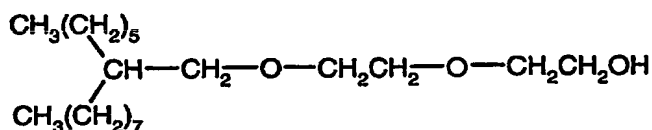


(Ia) [DAB25]

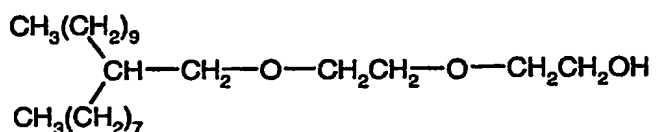




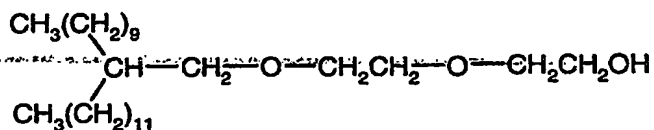
(Ib) [DAB50]



(Ic) [Aduxol GA7-02]



(Id) [Aduxol GA8-03]

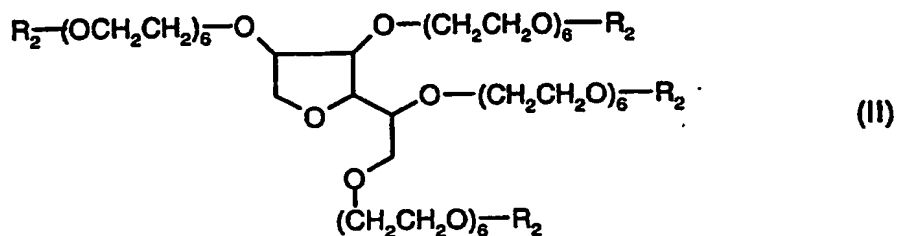


(Ie) [Aduxol-GA10-03]

Preferred sorbitan esters are esters of sorbitol or an ethoxylated sorbitan with a  $C_{12}$ - $C_{25}$ carboxylic acid.

Examples of  $C_{12}$ - $C_{25}$ carboxylic acids are lauric acid, oleic acid, palmitic acid or stearic acid. Esters of these carboxylic acids with sorbitol are commercially available from Fluka (Switzerland) as Span 20 (RTM) [sorbitan monolaurate], Span 40 (RTM) [sorbitan monopalmitate], Span 60 (RTM) [sorbitan monostearate], Span 65 (RTM) [sorbitan tristearate], Span 80 (RTM) [sorbitan monooleate] or Span 85 (RTM) [sorbitan trioleate].

A preferred ester of an ethoxylated sorbitan with a  $C_{12}$ - $C_{25}$ carboxylic acid is for example the compound of the formula II



wherein  $\text{R}_2$  is  $\text{C}_{12}$ - $\text{C}_{25}$ alkanoyl or  $\text{C}_{12}$ - $\text{C}_{25}$ alkenoyl.

Alkanoyl having 12 to 25 carbon atoms is a branched or unbranched radical, for example, dodecanoyl, tridecanoyl, tetradecanoyl, pentadecanoyl, hexadecanoyl, heptadecanoyl, octadecanoyl, icosanoyl or docosanoyl. Preference is given to alkanoyl having from 14 to 18 carbon atoms. Special preference is given to octadecanoyl (stearoyl).

Alkenoyl having 12 to 25 carbon atoms is a branched or unbranched radical comprising one or more carbon-carbon double bonds, for example, dodecenoyl, tridecenoyl, tetradecenoyl, pentadecenoyl, hexadecenoyl, heptadecenoyl or octadecenoyl. Preference is given to alkenoyl having from 14 to 18 carbon atoms. Special preference is given to octadecenyl (oleyl).

Fluorocarbons of special interest are for example semifluorinated surfactants like for example Du Pont Zonyl (RTM) fluorosurfactants. Examples of such compounds are Zonyl FSA (RTM) [ $\text{R}_\text{F}\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CO}_2\text{Li}$ ]; Zonyl FSN (RTM) [ $\text{R}_\text{F}\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2)_x\text{H}$ ]; or Zonyl TBS (RTM) [ $\text{R}_\text{F}\text{CH}_2\text{CH}_2\text{SO}_3\text{Y}$ ], wherein  $\text{R}_\text{F}$  is  $\text{F}(\text{CF}_2\text{CF}_2)_{3-8}$ , and Y is hydrogen or ammonium ( $\text{NH}_4^+$ ).

Siloxanes of special interest are for example polysiloxanes like for example those disclosed in Table A.

Table A: Examples of polysiloxanes

Code	Structure
DBE-224	PDMS-PEO block (75/25)
DBE-712	PDMS-PEO block (25/75)
DBE-814	PDMS-PEO block (20/80)
DBE-821	PDMS-PEO block (15/85)
DBP-732	PDMS-(PPO/60-PEO/40) block (30/70)
DMS-E12	EPCH <sub>2</sub> O(CH <sub>2</sub> ) <sub>3</sub> -PDMS-(CH <sub>2</sub> ) <sub>3</sub> OCH <sub>2</sub> EP (EPOXYPROPOXYPROPYL TERMINATED POLYDIMETHYLSILOXANE)
DMS-E21	EPCH <sub>2</sub> O(CH <sub>2</sub> ) <sub>3</sub> -PDMS-(CH <sub>2</sub> ) <sub>3</sub> OCH <sub>2</sub> EP
DMS-A12	H <sub>2</sub> N(CH <sub>2</sub> ) <sub>3</sub> -PDMS-(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub>
DMS-A21	H <sub>2</sub> N(CH <sub>2</sub> ) <sub>3</sub> -PDMS-(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub>

PDMS is polydimethylsiloxane.

PEO is polyethylene oxide.

EPCH<sub>2</sub>O is epoxypoxy.

PPO is polypropylene oxide.

Illustrative examples of polyolefins are:

1. Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, poly-4-methylpent-1-ene, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentene or norbornene, polyethylene (which optionally can be crosslinked), for example high density polyethylene (HDPE), high density and high molecular weight polyethylene (HDPE-HMW), high density and ultrahigh molecular weight polyethylene (HDPE-UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), (VLDPE) and (ULDPE).

Polyolefins, i.e. the polymers of monoolefins exemplified in the preceding paragraph, preferably polyethylene and polypropylene, can be prepared by different, and especially by the following, methods:

- a) radical polymerisation (normally under high pressure and at elevated temperature).
- b) catalytic polymerisation using a catalyst that normally contains one or more than one metal of groups IVb, Vb, VIb or VIII of the Periodic Table. These metals usually

have one or more than one ligand, typically oxides, halides, alcoholates, esters, ethers, amines, alkyls, alkenyls and/or aryls that may be either  $\pi$ - or  $\sigma$ -coordinated. These metal complexes may be in the free form or fixed on substrates, typically on activated magnesium chloride, titanium(III) chloride, alumina or silicon oxide. These catalysts may be soluble or insoluble in the polymerisation medium. The catalysts can be used by themselves in the polymerisation or further activators may be used, typically metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyloxanes, said metals being elements of groups Ia, IIa and/or IIIa of the Periodic Table. The activators may be modified conveniently with further ester, ether, amine or silyl ether groups. These catalyst systems are usually termed Phillips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or single site catalysts (SSC).

2. Mixtures of the polymers mentioned under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).

3. Copolymers of monoolefins and diolefins with each other or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/but-1-ene copolymers, propylene/isobutylene copolymers, ethylene/but-1-ene copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers and their copolymers with carbon monoxide or ethylene/acrylic acid copolymers and their salts (ionomers) as well as terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethylidene-norbornene; and mixtures of such copolymers with one another and with polymers mentioned in 1) above, for example polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers (EVA), LDPE/ethylene-acrylic acid copolymers (EAA), LLDPE/EVA, LLDPE/EAA and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides.

Preferably, the polyolefin is polyethylene or polypropylene or mixtures thereof.

Of interest is a process for the preparation of a polyolefin nanocomposite, wherein the filler is present in an amount of from 1 to 15%, preferably 1 to 10%, based on the weight of the polyolefin.

Also of interest is a process for the preparation of a polyolefin nanocomposite, wherein the non-ionic surfactant is present in an amount of from 0.1 to 7.5%, preferably 0.1 to 5%, based on the weight of the polyolefin.

Likewise of interest is a process for the preparation of a polyolefin nanocomposite, wherein the melt mixing of the components (polyolefin, filler and non-ionic surfactant) occurs between 120 and 290°C, preferably between 140 and 250°C, for example between 170 and 230°C.

The present process may comprise in addition, besides components (a), (b) and (c), further additives.

For example, the process of the invention may optionally also contain from 0.01 to 10%, preferably from 0.025 to 5%, and especially from 0.1 to 3% by weight of various conventional stabilizer coadditives, such as the materials listed below, or mixtures thereof.

## 1. Antioxidants

1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-( $\alpha$ -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.

1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

1.4. Tocopherols, for example  $\alpha$ -tocopherol,  $\beta$ -tocopherol,  $\gamma$ -tocopherol,  $\delta$ -tocopherol and mixtures thereof (vitamin E).

1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl)-isulfide.

1.6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-( $\alpha$ -methylcyclohexyl)-phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-( $\alpha$ -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-( $\alpha,\alpha$ -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-

tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

1.8. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl)malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)malonate, didodecylmercaptoethyl-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

1.9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

1.10. Triazine compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

1.11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.

1.12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

1.13. Esters of  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hy-

droxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.14. Esters of  $\beta$ -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane; 3,9-bis[2-{3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5.5]undecane.

1.15. Esters of  $\beta$ -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.17. Amides of  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazide, N,N'-bis[2-(3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyloxy)ethyl]oxamide (Nau-gard®XL-1, supplied by Uniroyal).

1.18. Ascorbic acid (vitamin C)



**1.19. Aminic antioxidants**, for example N,N'-di-isopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfamoyl)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylamino-phenol, 4-nonanoylamino-phenol, 4-dodecanoylamino-phenol, 4-octadecanoylamino-phenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis[(2-methylphenyl)amino]ethane, 1,2-bis(phenylamino)propane, (o-tolyl)biguanide, bis[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isohexyldiphenylamines, a mixture of mono- and dialkylated tert-butyl/diphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tert-octylphenothiazines, a mixture of mono- and dialkylated tert-octylphenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethylpiperid-4-yl)-hexamethylenediamine, bis(2,2,6,6-tetramethylpiperid-4-yl)sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol.

## **2. UV absorbers and light stabilisers**

**2.1. 2-(2'-Hydroxyphenyl)benzotriazoles**, for example 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis( $\alpha,\alpha$ -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-

(2-octyloxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)phenyl)benzotriazole, 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-ylphenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol 300;  $\left[ R-CH_2CH_2-COO-CH_2CH_2 \right]_2$ , where R = 3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-ylphenyl, 2-[2'-hydroxy-3'-( $\alpha,\alpha$ -dimethylbenzyl)-5'-(1,1,3,3-tetramethylbutyl)phenyl]-benzotriazole; 2-[2'-hydroxy-3'-(1,1,3,3-tetramethylbutyl)-5'-( $\alpha,\alpha$ -dimethylbenzyl)phenyl]benzotriazole.

2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

2.3. Esters of substituted and unsubstituted benzoic acids, for example 4-tert-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl)resorcinol, benzoyl resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2.4. Acrylates, for example ethyl  $\alpha$ -cyano- $\beta,\beta$ -diphenylacrylate, isooctyl  $\alpha$ -cyano- $\beta,\beta$ -diphenylacrylate, methyl  $\alpha$ -carbomethoxycinnamate, methyl  $\alpha$ -cyano- $\beta$ -methyl-p-methoxycinnamate, butyl  $\alpha$ -cyano- $\beta$ -methyl-p-methoxycinnamate, methyl  $\alpha$ -carbomethoxy-p-methoxycinnamate and N-( $\beta$ -carbomethoxy- $\beta$ -cyanovinyl)-2-methylindoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphe-

nylundecylketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitritotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)-malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearyloxy-2,2,6,6-tetramethylpiperidine, a condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensate of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]); a condensate of 1,6-hexanediamine and 2,4,6-trichloro-1,3,5-triazine as well as N,N-dibutylamine and 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [192268-64-7]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4,5]decane, a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro[4,5]decane and epichlorohydrin, 1,1-bis(1,2,2,6,6-pentamethyl-4-piperidyl-oxycarbonyl)-2-(4-methoxyphenyl)ethene, N,N'-bis-formyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine, a diester of 4-methoxymethylenemalonic acid with 1,2,2,6,6-

pentamethyl-4-hydroxypiperidine, poly[methylpropyl-3-oxy-4-(2,2,6,6-tetramethyl-4-piperidyl)]siloxane, a reaction product of maleic acid anhydride- $\alpha$ -olefin copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4-aminopiperidine.

2.7. Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide, mixtures of o- and p-methoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropoxy)phenyl]-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine, 2-[2-hydroxy-4-[3-(2-ethylhexyl-1-oxy)-2-hydroxypropyloxy]phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl)hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-diacetyl adipoyl dihydrazide, N,N'-bis(salicyloyl)oxalyl dihydrazide, N,N'-bis(salicyloyl)thiopropionyl dihydrazide.

4. Phosphites and phosphonites, for example triphenyl phosphite, diphenylalkyl phosphites, phenyldialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phos-

phite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,4-di-cumylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite, diisodecyl oxypentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, 6-isoctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl) methyl phosphite, bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, 2,2',2''-nitro-[triethyltris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite], 2-ethylhexyl(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite, 5-butyl-5-ethyl-2-(2,4,6-tri-tert-butylphenoxy)-1,3,2-dioxaphosphirane.

5. Hydroxylamines, for example, N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

6. Nitrones, for example, N-benzyl-alpha-phenylnitrone, N-ethyl-alpha-methylnitrone, N-octyl-alpha-heptylnitrone, N-lauryl-alpha-undecylnitrone, N-tetradecyl-alpha-tridecylnitrone, N-hexadecyl-alpha-pentadecylnitrone, N-octadecyl-alpha-heptadecylnitrone, N-hexadecyl-alpha-heptadecylnitrone, N-octadecyl-alpha-pentadecylnitrone, N-heptadecyl-alpha-heptadecylnitrone, N-octadecyl-alpha-hexadecylnitrone, nitrone derived from N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

7. Thiosynergists, for example, dilauryl thiodipropionate or distearyl thiodipropionate.

8. Peroxide scavengers, for example esters of  $\beta$ -thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutyldithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis( $\beta$ -dodecylmercapto)propionate.

9. Polyamide stabilisers, for example, copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

10. Basic co-stabilisers, for example, melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids, for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or zinc pyrocatecholate.

11. Nucleating agents, for example, inorganic substances, such as talcum, metal oxides, such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, preferably, alkaline earth metals; organic compounds, such as mono- or polycarboxylic acids and the salts thereof, e.g. 4-tert-butylbenzoic acid, adipic acid, diphenylacetic acid, sodium succinate or sodium benzoate; polymeric compounds, such as ionic copolymers (ionomers). Especially preferred are 1,3:2,4-bis(3',4'-dimethylbenzylidene)sorbitol, 1,3:2,4-di(paramethyl-dibenzylidene)sorbitol and 1,3:2,4-di(benzylidene)sorbitol.

12. Other additives, for example, plasticisers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flameproofing agents, antistatic agents and blowing agents.

13. Benzofuranones and indolinones, for example those disclosed in U.S. 4,325,863; U.S. 4,338,244; U.S. 5,175,312; U.S. 5,216,052; U.S. 5,252,643; DE-A-4316611; DE-A-4316622; DE-A-4316876; EP-A-0589839 or EP-A-0591102 or 3-[4-(2-acetoxyethoxy)-phenyl]-5,7-di-tert-butylbenzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]-benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(3,4-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(2,3-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one.

Of special interest is a process for the preparation of polyolefin nanocomposites which comprises as further additives phenolic antioxidants, light-stabilizers, processing stabilizers, sol-

vents, pigments, dyes, plasticizers, compatibilizers, toughening agents, thixotropic agents, levelling assistants and/or metal passivators.

The mixing of components (a) (b) and (c) and optionally further additives is done by commonly used techniques such as roll-milling, mixing in a Banbury type mixer, or mixing in an extruder barrel and the like.

X ray diffraction analysis shows that the non-ionic surfactants interact with the filler like for example the layered silicate clays. The non-ionic surfactants intercalate and partially exfoliate the clay structure when added to the clay in a polyolefin melt. Most importantly, there is no requirement to preintercalate the clay with an additive.

The polyolefin nanocomposites obtained according to the process of the present invention possess properties and applications associated with polyolefin nanocomposites. These properties include improved heat distortion temperature, improved fire retardancy, improved gas barrier, enhanced stiffness and dimensional stability, and improved mechanical properties like for example higher tensile modulus and a tensile strength which are similar or higher than a polyolefin matrix phase alone. The polyolefin nanocomposites obtained according to the process of the present invention possess also improved homogeneity and/or transparency, and improved wettability which improves dyeability or printability of the polyolefin.

Of interest is a process for the preparation of a polyolefin nanocomposite which comprises melt mixing a mixture of a polyolefin, a filler and a non-ionic surfactant, wherein the filler is an unmodified filler.

The mixture of the filler and the non-ionic surfactant, and where applicable further additives, may also be added to the polyolefin in the form of a master batch that contains the mixture in a concentration of, for example, from 2.5 to 40% by weight. This master batch is then heated with a polyolefin to form a polyolefin nanocomposite.

Preferably the filler and the non-ionic surfactant, and where applicable further additives, are precompounded before melt blending with a polyolefin.

The present invention also relates to polyolefin nanocomposites obtained by melt mixing a mixture of a polyolefin, a filler and a non-ionic surfactant.

A further embodiment of the present invention is a nanocomposite comprising

- a) a polyolefin which is susceptible to oxidative, thermal or light-induced degradation,
- b) a filler,
- c) a non-ionic surfactant, and
- d) an additive selected from the group consisting of phenolic antioxidants, light-stabilizers, processing stabilizers, solvents, pigments, dyes, plasticizers, compatibilizers, toughening agents, thixotropic agents, levelling assistants and metal passivators or mixtures thereof.

Preferably, component (d) is a phenolic antioxidant, light-stabilizer, processing stabilizer and metal passivator or mixtures thereof.

The preferred non-ionic surfactants, fillers and polyolefins are the same as those described in the process for the preparation of the polyolefin nanocomposites.

The polyolefin nanocomposites according to the invention may be used in an extremely wide variety of forms, e.g. in the form of films, fibres, tapes, moulding compounds or profiles, or as binders for surface-coatings, especially powder coatings, adhesives or cements.

The polyolefin nanocomposites according to the invention may likewise be used in an extremely wide variety of forms, especially in the form of thick-layer polyolefin moulded articles that are in lasting contact with extracting media, such as, for example, pipes for liquids or gases, films, fibres, geomembranes, tapes, profiles or tanks.

The polyolefin nanocomposites according to the invention can be advantageously used for the preparation of various shaped articles. Examples are:

I-1) Floating devices, marine applications, pontoons, buoys, plastic lumber for decks, piers, boats, kayaks, oars, and beach reinforcements.



I-2) Automotive applications, in particular bumpers, dashboards, battery, rear and front linings, moldings parts under the hood, hat shelf, trunk linings, interior linings, air bag covers, electronic moldings for fittings (lights), panes for dashboards, headlamp glass, instrument panel, exterior linings, upholstery, automotive lights, head lights, parking lights, rear lights, stop lights, interior and exterior trims; door panels; gas tank; glazing front side; rear windows; seat backing, exterior panels, wire insulation, profile extrusion for sealing, cladding, pillar covers, chassis parts, exhaust systems, fuel filter / filler, fuel pumps, fuel tank, body side mouldings, convertible tops, exterior mirrors, exterior trim, fasteners / fixings, front end module, glass, hinges, lock systems, luggage / roof racks, pressed/stamped parts, seals, side impact protection, sound deadener / insulator and sunroof.

I-3) Road traffic devices, in particular sign postings, posts for road marking, car accessories, warning triangles, medical cases, helmets, tires.

I-4) Devices for plane, railway, motor car (car, motorbike) including furnishings.

I-5) Devices for space applications, in particular rockets and satellites, e.g. reentry shields.

I-6) Devices for architecture and design, mining applications, acoustic quietized systems, street refuges, and shelters.

II-1) Appliances, cases and coverings in general and electric/electronic devices (personal computer, telephone, portable phone, printer, television-sets, audio and video devices), flower pots, satellite TV bowl, and panel devices.

II-2) Jacketing for other materials such as steel or textiles.

II-3) Devices for the electronic industry, in particular insulation for plugs, especially computer plugs, cases for electric and electronic parts, printed boards, and materials for electronic data storage such as chips, check cards or credit cards.

II-4) Electric appliances, in particular washing machines, tumblers, ovens (microwave oven), dish-washers, mixers, and irons.

**II-5) Covers for lights (e.g. street-lights, lamp-shades).**

**II-6) Applications in wire and cable (semi-conductor, insulation and cable-jacketing).**

**II-7) Foils for condensers, refrigerators, heating devices, air conditioners, encapsulating of electronics, semi-conductors, coffee machines, and vacuum cleaners.**

**III-1) Technical articles such as cogwheel (gear), slide fittings, spacers, screws, bolts, handles, and knobs.**

**III-2) Rotor blades, ventilators and windmill vanes, solar devices, swimming pools, swimming pool covers, pool liners, pond liners, closets, wardrobes, dividing walls, slat walls, folding walls, roofs, shutters (e.g. roller shutters), fittings, connections between pipes, sleeves, and conveyor belts.**

**III-3) Sanitary articles, in particular shower cubicles, lavatory seats, covers, and sinks.**

**III-4) Hygienic articles, in particular diapers (babies, adult incontinence), feminine hygiene articles, shower curtains, brushes, mats, tubs, mobile toilets, tooth brushes, and bed pans.**

**III-5) Pipes (cross-linked or not) for water, waste water and chemicals, pipes for wire and cable protection, pipes for gas, oil and sewage, guttering, down pipes, and drainage systems.**

**III-6) Profiles of any geometry (window panes) and siding.**

**III-7) Glass substitutes, in particular extruded plates, glazing for buildings (monolithic, twin or multiwall), aircraft, schools, extruded sheets, window film for architectural glazing, train, transportation, sanitary articles, and greenhouse.**

**III-8) Plates (walls, cutting board), extrusion-coating (photographic paper, tetrapack and pipe coating), silos, wood substitute, plastic lumber, wood composites, walls, surfaces, furniture, decorative foil, floor coverings (interior and exterior applications), flooring, duck boards, and tiles.**

**III-9) Intake and outlet manifolds.**

**III-10) Cement-, concrete-, composite-applications and covers, siding and cladding, hand rails, banisters, kitchen work tops, roofing, roofing sheets, tiles, and tarpaulins.**

**IV-1) Plates (walls and cutting board), trays, artificial grass, astroturf, artificial covering for stadium rings (athletics), artificial floor for stadium rings (athletics), and tapes.**

**IV-2) Woven fabrics continuous and staple, fibers (carpets / hygienic articles / geotextiles / monofilaments; filters; wipes / curtains (shades) / medical applications), bulk fibers (applications such as gown / protection clothes), nets, ropes, cables, strings, cords, threads, safety seat-belts, clothes, underwear, gloves; boots; rubber boots, intimate apparel, garments, swimwear, sportswear, umbrellas (parasol, sunshade), parachutes, paraglides, sails, "balloon-silk", camping articles, tents, airbeds, sun beds, bulk bags, and bags.**

**IV-3) Membranes, insulation, covers and seals for roofs, tunnels, dumps, ponds, dumps, walls roofing membranes, geomembranes, swimming pools, curtains (shades) / sun-shields, awnings, canopies, wallpaper, food packing and wrapping (flexible and solid), medical packaging (flexible & solid), airbags/safety belts, arm- and head rests, carpets, centre console, dashboard, cockpits, door, overhead console module, door trim, headliners, interior lighting, interior mirrors, parcel shelf, rear luggage cover, seats, steering column, steering wheel, textiles, and trunk trim.**

**V) Films (packaging, dump, laminating, agriculture and horticulture, greenhouse, mulch, tunnel, silage), bale wrap, swimming pools, waste bags, wallpaper, stretch film, raffia, desalination film, batteries, and connectors.**

**VI-1) Food packing and wrapping (flexible and solid), bottles.**

**VI-2) Storage systems such as boxes (crates), luggage, chest, household boxes, pallets, shelves, tracks, screw boxes, packs, and cans.**

VI-3) Cartridges, syringes, medical applications, containers for any transportation, waste baskets and waste bins, waste bags, bins, dust bins, bin liners, wheely bins, container in general, tanks for water / used water / chemistry / gas / oil / gasoline / diesel; tank liners, boxes, crates, battery cases, troughs, medical devices such as piston, ophthalmic applications, diagnostic devices, and packing for pharmaceuticals blister.

VII-1) Extrusion coating (photo paper, tetrapack, pipe coating), household articles of any kind (e.g. appliances, thermos bottle / clothes hanger), fastening systems such as plugs, wire and cable clamps, zippers, closures, locks, and snap-closures.

VII-2) Support devices, articles for the leisure time such as sports and fitness devices, gymnastics mats, ski-boots, inline-skates, skis, big foot, athletic surfaces (e.g. tennis grounds); screw tops, tops and stoppers for bottles, and cans.

VII-3) Furniture in general, foamed articles (cushions, impact absorbers), foams, sponges, dish clothes, mats, garden chairs, stadium seats, tables, couches, toys, building kits (boards / figures / balls), playhouses, slides, and play vehicles.

VII-4) Materials for optical and magnetic data storage.

VII-5) Kitchen ware (eating, drinking, cooking, storing).

VII-6) Boxes for CD's, cassettes and video tapes; DVD electronic articles, office supplies of any kind (ball-point pens, stamps and ink-pads, mouse, shelves, tracks), bottles of any volume and content (drinks, detergents, cosmetics including perfumes), and adhesive tapes.

VII-7) Footwear (shoes / shoe-soles), insoles, spats, adhesives, structural adhesives, food boxes (fruit, vegetables, meat, fish), synthetic paper, labels for bottles, couches, artificial joints (human), printing plates (flexographic), printed circuit boards, and display technologies.

VII-8) Devices of filled polymers (talc, chalk, china clay (kaolin), wollastonite, pigments, carbon black,  $\text{TiO}_2$ , mica, nanocomposites, dolomite, silicates, glass, asbestos).

Thus, a further embodiment of the present invention relates to a shaped article, in particular a film, pipe, profile, bottle, tank or container, fiber containing a polyolefin nanocomposite as described above.

A film is preferred. The film can be prepared as a blown film cast film or via extrusion coating. Especially preferred is a multilayer film.

A further embodiment of the present invention relates to a molded article containing a polyolefin nanocomposite as described above. The molding is in particular effected by injection, blow, compression, roto-molding or slush-molding or extrusion.

A preferred embodiment of the present invention is likewise the use of a non-ionic surfactant to intercalate and exfoliate a filler and disperse the filler in a polyolefin matrix to form a nanocomposite.

The preferred non-ionic surfactants, fillers and polyolefins are the same as those described in the process for the preparation of the polyolefin nanocomposites.

The following examples illustrate the invention further. Parts or percentages relate to weight.

**Example 1:** Preparation of polypropylene nanocomposites in a batch mixer.

50 g of polypropylene [Basell KY 6100 (RTM)], was blended with 0.25 % of Irganox 1010 (RTM) (pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]) and 0.25 % of Irgafos 168 (RTM) (tris(2,4-di-tert-butylphenyl) phosphite), 5 % of a montmorillonite clay [Cloisite (Na<sup>+</sup>) (RTM) obtained from Southern Clay Industries] and 2.5 % of a non-ionic surfactant according to Table 1 in a plastic cup and then added to a batch mixer operating at 25 rpm and 180°C, the mixture was then taken to 50 rpm for 10 minutes. Small scale injection moulding was performed with a CS-183MMX Minimax moulder. The mixing chamber was preheated to 230°C and the mould was oven heated to 120°C for one hour prior to injection moulding. Approximately 5 g of the material was placed in the mixing chamber and heated for 4 to 5 minutes. A small shot was taken from the CS-183MMX Minimax moulder prior to placing the mould in position. Six tensile bars with the dimensions 18 mm by 5 mm by 0.85 mm were produced for each of the 5 g material.

Tensile testing was performed according to ASTM D 638 with a Rheometrics mini material tensile tester [Minimat 2000 (RTM)] equipped with a 1000 N load cell (40 mm/min). The results are summarized in Table 1.

Table 1:

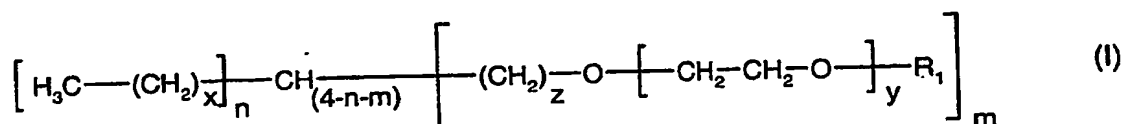
Example	Non-ionic surfactant	d-001 in Å <sup>c)</sup>	Normalized Modulus of Elasticity <sup>e)</sup>
1a <sup>a)</sup>	none	10	1.12
1b <sup>b)</sup>	Nafol 1822 + 2EO <sup>d)</sup>	13	1.16
1c <sup>b)</sup>	PE-b-PEO (MW 920) <sup>f)</sup>	17	1.25
1d <sup>b)</sup>	PE-b-PEO (MW 1400) <sup>g)</sup>	14	1.20
1e <sup>b)</sup>	Aduxol GA8-03 <sup>h)</sup>	13.4	1.16
1f <sup>b)</sup>	Aduxol GA10-03 <sup>h)</sup>	13.3	1.20
1g <sup>b)</sup>	Aduxol GA7-02 <sup>h)</sup>	13.7	1.11
1h <sup>b)</sup>	DAB25 <sup>k)</sup>	13.6	1.16
1i <sup>b)</sup>	DAB50 <sup>l)</sup>	14.7	1.20

a) Comparative Example.

b) Example according to the invention.

c) Interlayer distance determined by X-ray diffraction.

d) Nafol 1822 + 2EO is a linear polyethylene-block-poly(ethylene oxide) of the formula I:



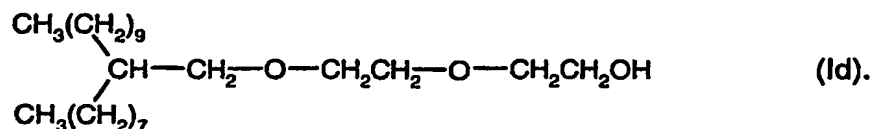
wherein m is 1, n is 1, average x is 20, average y is 2, z is 0, and R<sub>1</sub> is hydrogen.

e) Normalized modulus of elasticity relative to polypropylene processed under similar conditions (=1.0).

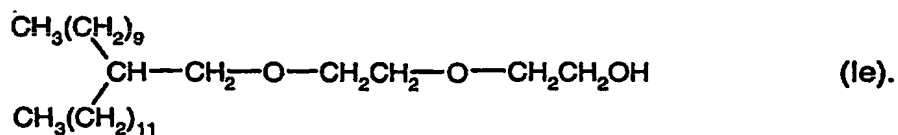
f) PE-b-PEO (MW 920) (RTM) is a linear polyethylene-block-poly(ethylene oxide) of the formula I, wherein m is 1, n is 1, average x is 32, average y is 10, z is 0, and R<sub>1</sub> is hydrogen.

g) PE-b-PEO (MW 1400) (RTM) is a linear polyethylene-block-poly(ethylene oxide) of the formula I, wherein m is 1, n is 1, average x is 50, average y is 15, z is 0, and R<sub>1</sub> is hydrogen.

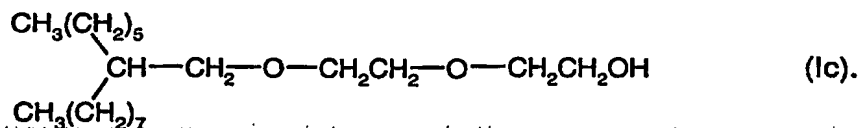
h) Aduxol GA8-03 (RTM) is a compound of the formula Id



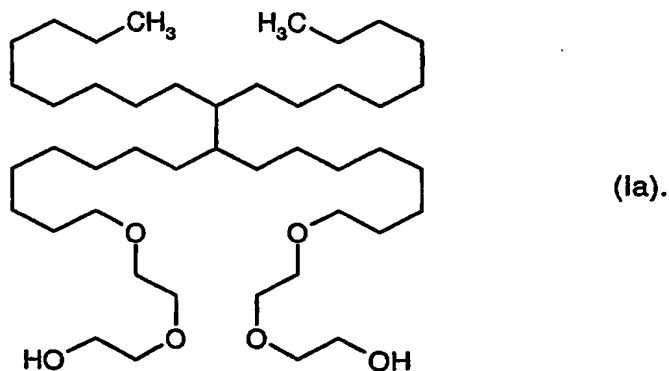
i) Aduxol GA10-03 (RTM) is a compound of the formula Ie



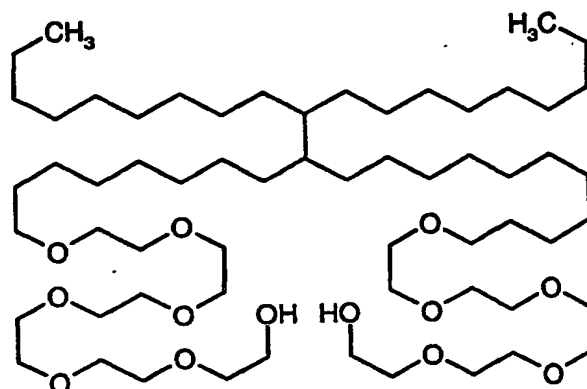
j) Aduxol GA7-02 (RTM) is a compound of the formula Ic



k) DAB25 (RTM) is a compound of the formula Ia



l) DAB50 (RTM) is a compound of the formula Ib



(1b)

The X-ray diffraction (XRD) spectra show that all non-ionic surfactants according to Table 1 intercalate the used clay in the direct melt blending experiments in the batch mixer. This is demonstrated by an increase in d-spacing – the spacing between clay layers – from 10 Å to 13 – 17 Å. The elasticity modulus of samples is enhanced 4 - 25% over polypropylene.

**Example 2:** Preparation of polypropylene nanocomposites in a batch mixer.

Nanocomposites were prepared as described in Example 1 but with 2.5% of a non-ionic surfactant according to Table 2.

Table 2:

Example	Non-ionic surfactant	d-001 in Å <sup>c)</sup>	Normalized Modulus of Elasticity <sup>d)</sup>
2a <sup>a)</sup>	none	10	1.12
2b <sup>b)</sup>	DBE 224 (RTM) <sup>e)</sup>	14	1.32
2c <sup>b)</sup>	DBE 821 (RTM) <sup>1)</sup>	17	1.32
2d <sup>b)</sup>	Tegomer ME 1010 (RTM) <sup>9)</sup>	17.3	1.36

- a) Comparative Example.
- b) Example according to the invention.
- c) Interlayer distance determined by X-ray diffraction.
- d) Normalized modulus of elasticity relative to polypropylene processed under similar conditions (=1.0).
- e) DBE 224 (RTM) is dimethylsiloxane-ethylene oxide-block copolymer (25% non siloxane, MW 10000), commercially available from ABCR GmbH & Co KG (Karlsruhe, Germany).



- f) DBE 821 (RTM) is dimethylsiloxane-ethylene oxide-block copolymer (85% non siloxane, MW3600), commercially available from ABCR GmbH & Co KG (Karlsruhe, Germany).
- g) Tegomer ME 1010 (RTM) is polymethyl methacrylate-block-polyoxyethylene copolymer, commercially available from Goldschmidt AG (Essen, Germany).

The X-ray diffraction (XRD) spectra show that all non-ionic surfactants according to Table 2 intercalate the used clay in the direct melt blending experiments in the batch mixer. This is demonstrated by an increase in d-spacing – the spacing between clay layers – from 10 Å to 14 – 17 Å. The elasticity modulus of samples is enhanced 32 - 36% over polypropylene.

**Example 3:** Preparation of polypropylene nanocomposites in a batch mixer.

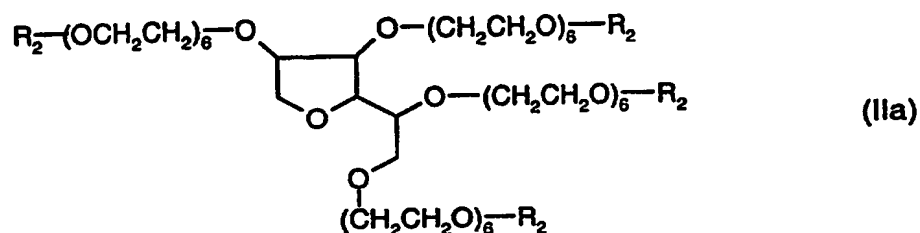
Nanocomposites were prepared as described in Example 1 but with 2.5% of a non-ionic surfactant according to Table 3.

Table 3:

Example	Non-ionic surfactant	d-001 in Å <sup>c)</sup>	Normalized Modulus of Elasticity <sup>d)</sup>
3a <sup>a)</sup>	none	10	1.12
3b <sup>b)</sup>	Sorbitan monooleate	13.7	1.32
3c <sup>b)</sup>	Sorbitan trioleate	12	1.21
3d <sup>b)</sup>	Sorbitan monostearate	13.7	1.36
3e <sup>b)</sup>	Ethoxylated sorbitan ester <sup>a)</sup>	12	1.16

- a) Comparative Example.
- b) Example according to the invention.
- c) Interlayer distance determined by X-ray diffraction.
- d) Normalized modulus of elasticity relative to polypropylene processed under similar conditions (=1.0).

e) Ethoxylated sorbitan ester is a compound of the formula IIa

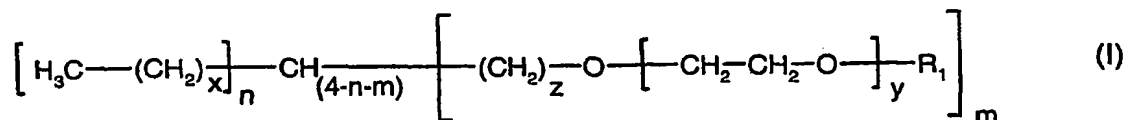


wherein R<sub>2</sub> is C<sub>18</sub>alkanoyl.

The X-ray diffraction (XRD) spectra show that all non-ionic surfactants according to Table 3 intercalate the used clay in the direct melt blending experiments in the batch mixer. This is demonstrated by an increase in d-spacing – the spacing between clay layers – from 10 Å to 12 – 14 Å. The elasticity modulus of samples is enhanced 16 - 36% over polypropylene.

**What is claimed is:**

1. A process for the preparation of a polyolefin nanocomposite which comprises melt mixing a mixture of a) a polyolefin, b) a filler and c) a non-ionic surfactant.
2. A process according to claim 1, wherein the filler is a natural or synthetic phyllosilicate or a mixture of such phyllosilicates.
3. A process according to claim 1, wherein the filler is a layered silicate clay.
4. A process according to claim 1, wherein the filler is a montmorillonite, bentonite, beidelite, mica, hectorite, saponite, nontronite, sauconite, vermiculite, ledikite, magadite, kenyaite, stevensite, volkonskoite or a mixture thereof.
5. A process according to claim 1, wherein the non-ionic surfactant is a block or graft copolymer containing a hydrophilic and a hydrophobic segment which do not contain an onium functionality.
6. A process according to claim 5, wherein the hydrophilic segment is a poly(ethylene oxide) block and the hydrophobic segment is a branched or unbranched polyolefin, a fluorocarbon, a siloxane or a low molecular weight methacrylate.
7. A process according to claim 1, wherein the non-ionic surfactant is a sorbitan ester, a dimethylsiloxane-ethylene oxide-block copolymer, a poly(methyl methacrylate)-block-poly(oxyethylene) copolymer or a compound of the formula I



wherein

m is 1 or 2,

n is 1 or 2,

x is greater than or equal to 1,

y is greater than or equal to 1,  
z is greater than or equal to 0, and  
R<sub>1</sub> is hydrogen or C<sub>1</sub>-C<sub>25</sub>alkyl.

8. A process according to claim 7, wherein the sorbitan ester is an ester of sorbitol or an ethoxylated sorbitan with a C<sub>12</sub>-C<sub>25</sub>carboxylic acid.

9. A process according to claim 1, wherein the polyolefin is polyethylene or polypropylene or mixtures thereof.

10. A process according to claim 1, wherein the filler is present in an amount of from 1 to 15 %, based on the weight of the polyolefin.

11. A process according to claim 1, wherein the non-ionic surfactant is present in an amount of from 0.1 to 7.5 %, based on the weight of the polyolefin.

12. A process according to claim 1, wherein the melt mixing occurs between 120 and 290°C.

13. A process according to claim 1, comprising in addition, besides components (a), (b) and (c), further additives.

14. A process according to claim 13, comprising as further additives phenolic antioxidants, light-stabilizers, processing stabilizers, solvents, pigments, dyes, plasticizers, compatibilizers, toughening agents, thixotropic agents, levelling assistants and/or metal passivators.

15. A polyolefin nanocomposite obtained by a process according to claim 1.

16. A nanocomposite comprising

- a) a polyolefin which is susceptible to oxidative, thermal or light-induced degradation,
- b) a filler,
- c) a non-ionic surfactant, and
- d) an additive selected from the group consisting of phenolic antioxidants, light-stabilizers, processing stabilizers, solvents, pigments, dyes, plasticizers, compatibilizers,

toughening agents, thixotropic agents, levelling assistants and metal passivators or mixtures thereof.

17. Use of a non-ionic surfactant to intercalate and exfoliate a filler and disperse the filler in a polyolefin matrix to form a nanocomposite.

**Abstract of the Disclosure**

The instant invention discloses a process for the preparation a polyolefin nanocomposite which comprises melt mixing a mixture of a polyolefin, a filler and a non-ionic surfactant.

PCT Application

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